Lifetime Quantification of Coated Metallic ICs

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Lifetime Quantification of Coated Metallic ICs

- Long term structural integrity of metallic ICs – Focus of this talk
  - Interfacial strength quantification
  - IC life/durability prediction
- Effects of IC creep on flow channel long term geometry changes – Global study – Documented in PNNL Report No. 16342
- Influence of mesh current collector/contact paste mechanical properties on stack performance – Global study – Part of tomorrow's talk

Lifetime Quantification of Coated Metallic ICs

- Technical objectives:
  - To predict lifetime of metallic interconnect materials with and without spinel coating;
  - To evaluate lifetime of different candidate IC materials based on experimentally available test results;
  - To control subscale growth kinetics by optimizing spinel coating thickness to meet SECA life requirement.

Technical Approaches

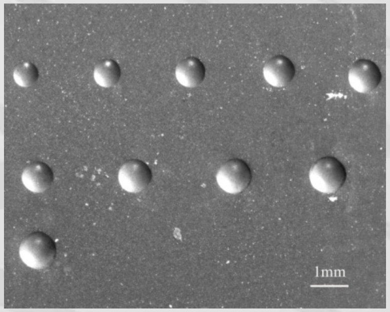
- Quantify strength of various interfaces by an integrated experimental/analytical approach;
- Experimentally quantify/predict subscale oxide growth kinetics for various coating thickness;
- Predict stresses on various interfaces for coated IC generated during isothermal cooling and thermal cycling;
- Predict interconnect life by comparing stress and strength at various interfaces;
- Explore possible approaches to improve coated IC life:
  - Improve interfacial strength by surface modification;
  - Reduce shear stress at the interface by reducing substrate thickness
  - Rare-earth-doped coating to improve grain boundary strengthen → delay delamination – Examined experimentally at PNNL

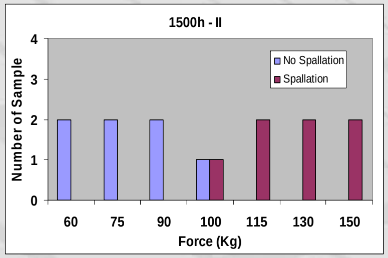
Interfacial Strength Quantification and IC Life Prediction – Progress to Date

Accomplishments:

- Identified the interfacial failure driving force at various interfaces
- Quantified the strength of the following interfaces:
  - Oxide/Crofer22
  - Oxide/Spinel coating
  - Oxide/SS441
- Predicted Crofer22 life under isothermal cooling with and without spinel coating
- Explore the possibility of using finer surface finish to improve the adhesion strength between oxide and SS441
- Detailed finite element analyses of the SS441/oxide interface considering surface defects
- Explore possible reasons of de-cohesion through grain boundary analyses

Technical Flow Chart – IC Life Prediction





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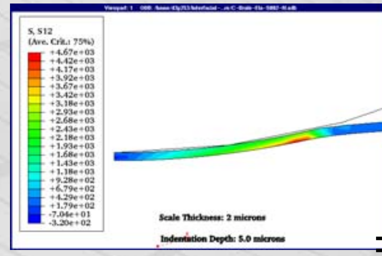

Oxide/substrate interfacial strength =>

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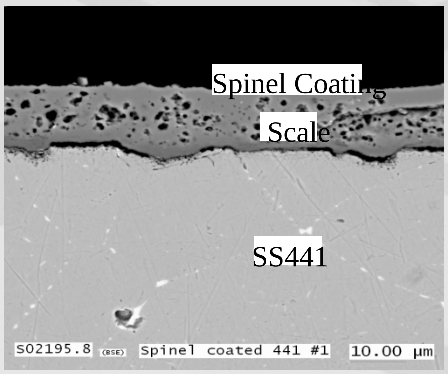

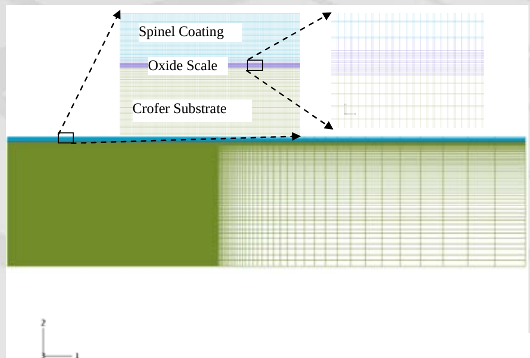

Oxide/Spinel coating =>interfacial strength

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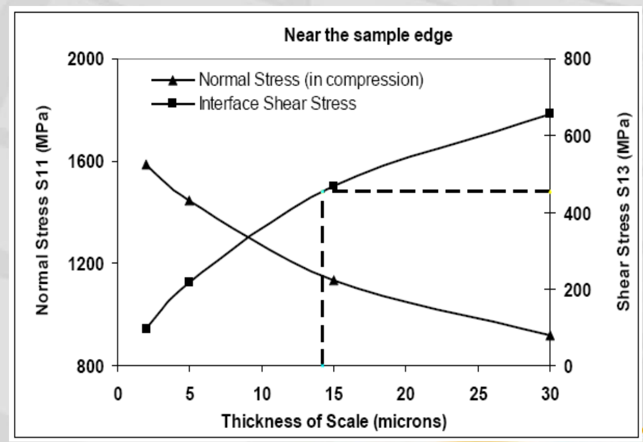

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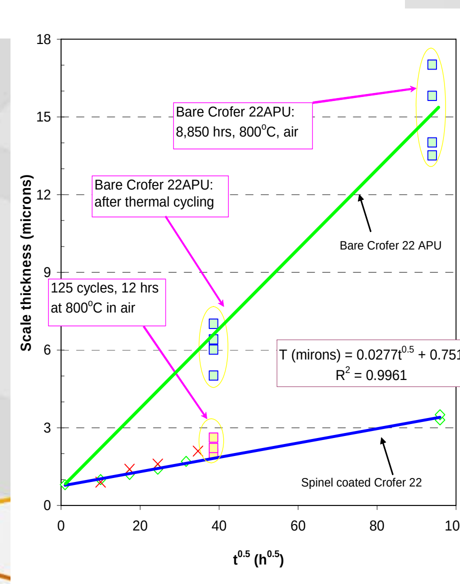
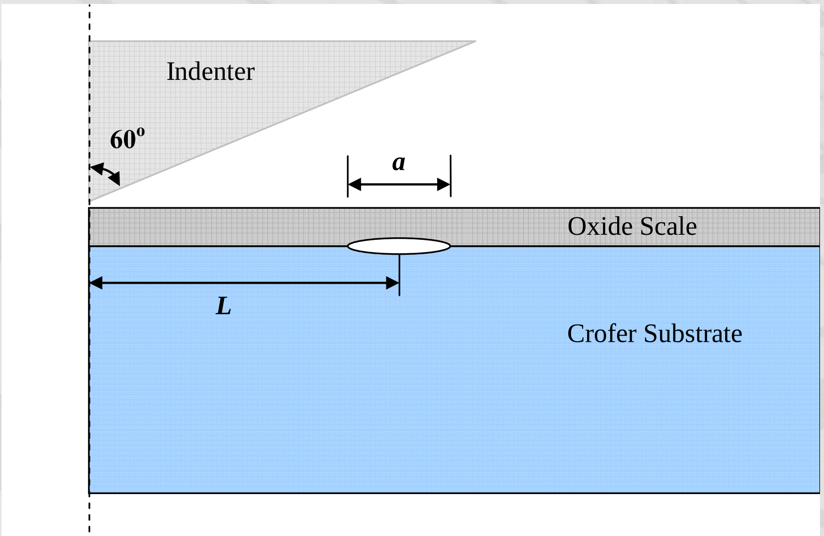
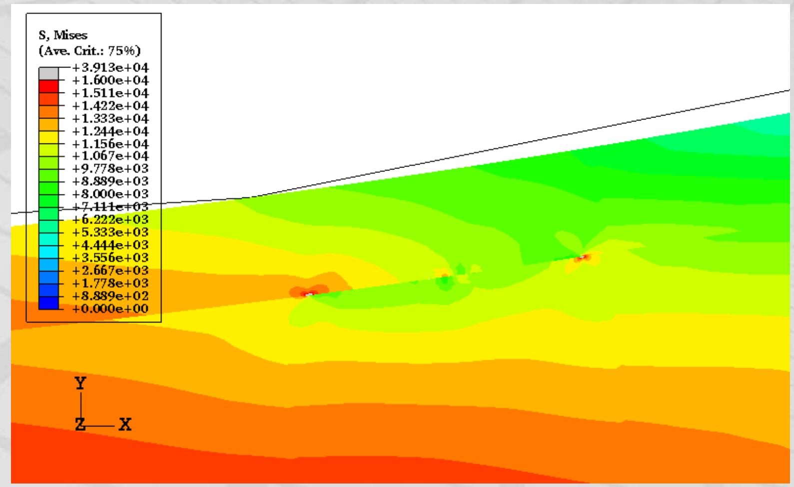
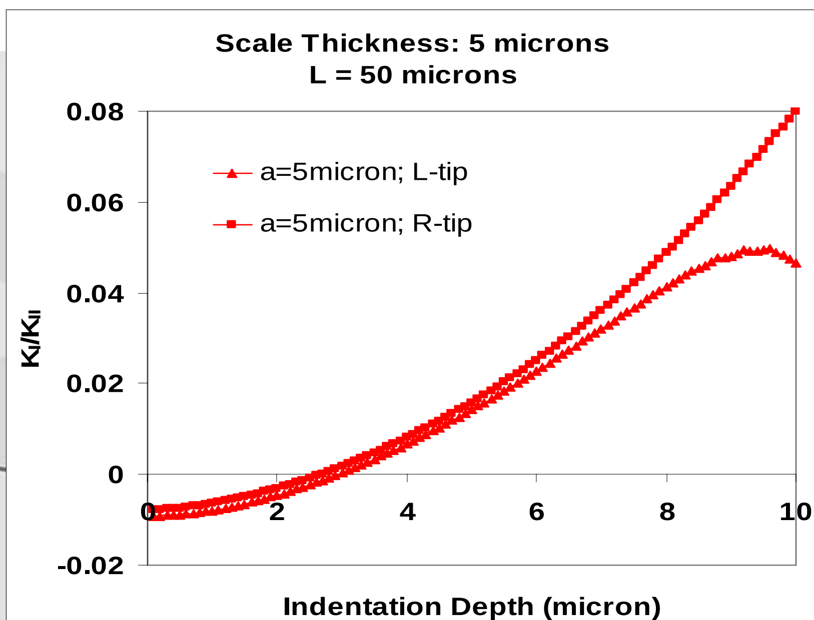


IC life prediction <=

Identification of Interfacial Failure Driving Force – Interfacial Shear Stress







- Integrate experimental indentation tests and finite element indentation simulation to quantify interfacial strength at different interfaces

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Interfacial Strength Quantification - Crofer

Indentation tests utilizing 1/16" Rockwell ball indenter; Oxidized Crofer Samples

Spec.#	Scale Thick	Load (kgf) 60 No	60 Yes	75 No	75 Yes	90 No	90 Yes	100 No	100 Yes	115 No	115 Yes	130 No	130 Yes	150 No	150 Yes
1	1.38	2		2		2		3		2	1	2		2	1
2	1.50	3		3		3		3		2		3		3	
3	2.04	2		2		2		2		2		2		2	
4	2.06	1		1		1		1		2		2	1	2	
5	2.41	2		2		2		1	1		2		2		2
6	2.71	3		3		3		2	1	2	1	1	2	1	2
7	2.96	3		2		1	1	1	2	1	1		1		2

- Maximum interfacial strength between Crofer/Oxide: 395Mpa
- Interfacial strength decreases with scale growth

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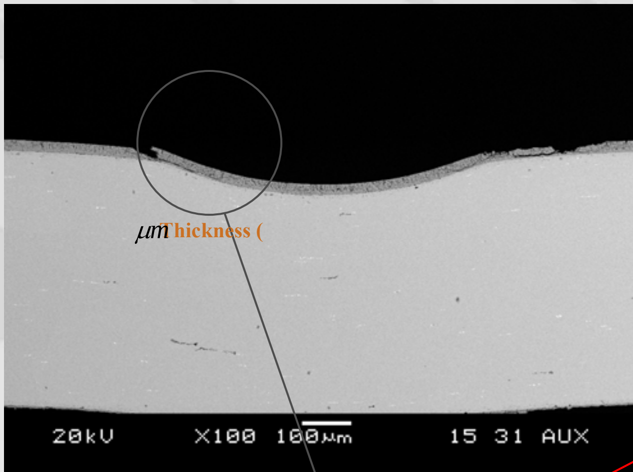
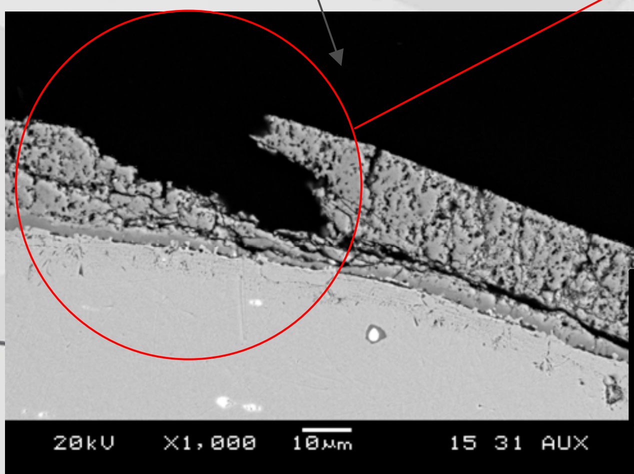
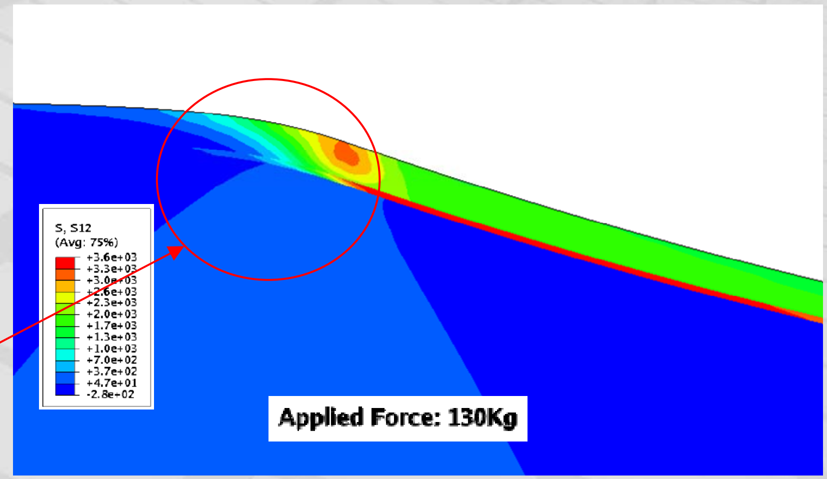
Experimental Indentation Tests on Coated Crofer22 Tri-layer System

Spinel-coated Crofer illustrating failure occurring at spinel/oxide interface. Failure load was 60kgf utilizing 1/16” ball indenter.







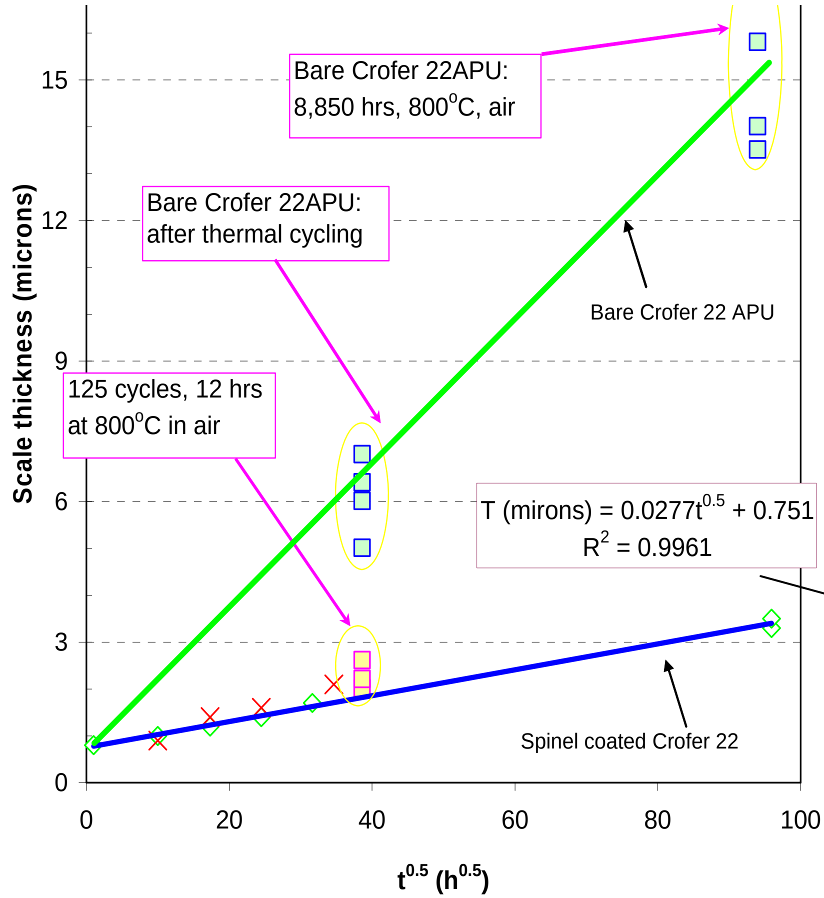
- Maximum interfacial strength between Spinel coating/Oxide: 886Mpa

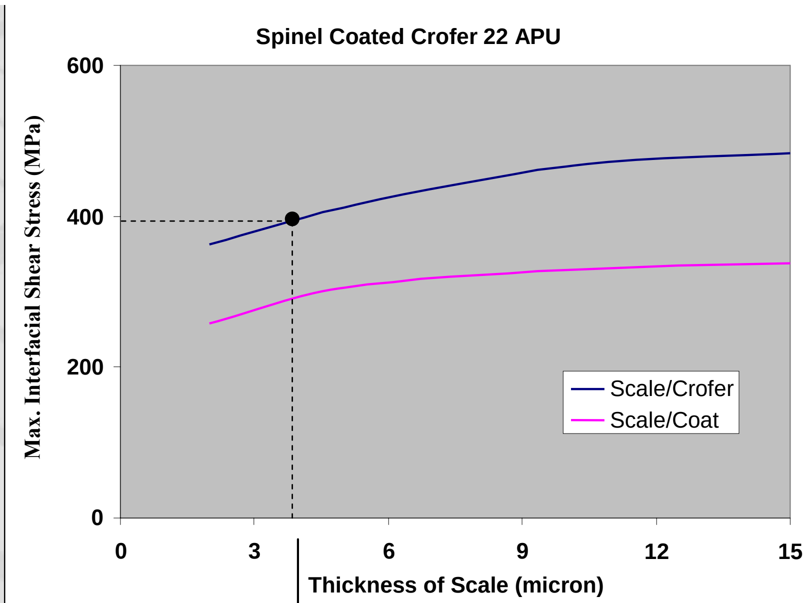
Experimental indentation results on Crofer 22 tri-layer system

			Load (Kgf)													
	)		60		75		90		100		115		130		150	
Spec #	scale	coat	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall
1	1.50	12.93	7	0	4	3	3	4	0	7	0	7	0	7	0	7
2	1.85	19.80	3	0	2	0	5	5	3	5	0	5	-	-	-	-

Life Prediction for Coated Crofer Tri-Layer System

Oxide growth kinetics for Crofer with 15-micron spinel coating





Predicted life = 15504 h

Indentation Results for Oxidized SS441 in As-Received Condition

		Load (Kgf)													
		60		75		90		100		115		130		150	
Spec #	Scale Thickness (μm)	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall	No Spall	Spall
1	0.89	-	-	-	-	2	0	6	0	7	0	6	1	5	3
2	1.13	2	0	1	1	0	1	1	0	0	1	0	1	1	1
3	1.66	7	2	3	7	0	8	0	6	0	3	0	2	0	2
4	2.08	4	1	5	0	3	0	3	2	3	2	2	3	2	9
5	2.32	4	1	3	2	3	3	0	4	0	4	0	4	6	2
6	3.35	2	2	3	1	1	2	2	1	2	1	1	2	4	2
7	3.94	3	1	2	1	2	3	2	5	3	1	2	1	2	4

- Inconsistent indentation results;
- Maximum interfacial strength between oxide/SS441- as received: 320Mpa

Effects of Surface Finish on Consistency of Indentation Results

Crofer

Profile #	$R_a\ (\mu m)$	$R_y\ (\mu m)$	$R_q\ (\mu m)$	$R_z\ (\mu m)$
1	0.25	1.69	1.61	0.31
2	0.25	1.82	1.64	0.32
3	0.27	2.14	1.78	0.34
4	0.32	2.51	2.02	0.39
5	0.31	2.21	2.20	0.38
6	0.35	2.25	2.07	0.44
7	0.26	1.97	1.70	0.32
Average	0.29	2.08	1.86	0.36

Effects of Surface Finish on Consistency of Indentation Results

SS441- as received

Profile #	$R_a\ (\mu m)$	$R_y\ (\mu m)$	$R_q\ (\mu m)$	$R_z\ (\mu m)$
1	0.85	8.96	5.48	1.21
2	0.67	5.33	4.60	0.84
3	0.66	6.20	4.77	0.82
Average	0.73	6.83	4.95	0.96

Effective range for indentation tests:

$$H_o / R_a < 5.2$$

Life Prediction for Coated SS441 Tri-Layer System with Various Coating Thickness

•Interfacial strength of oxide/SS441: 320MPa

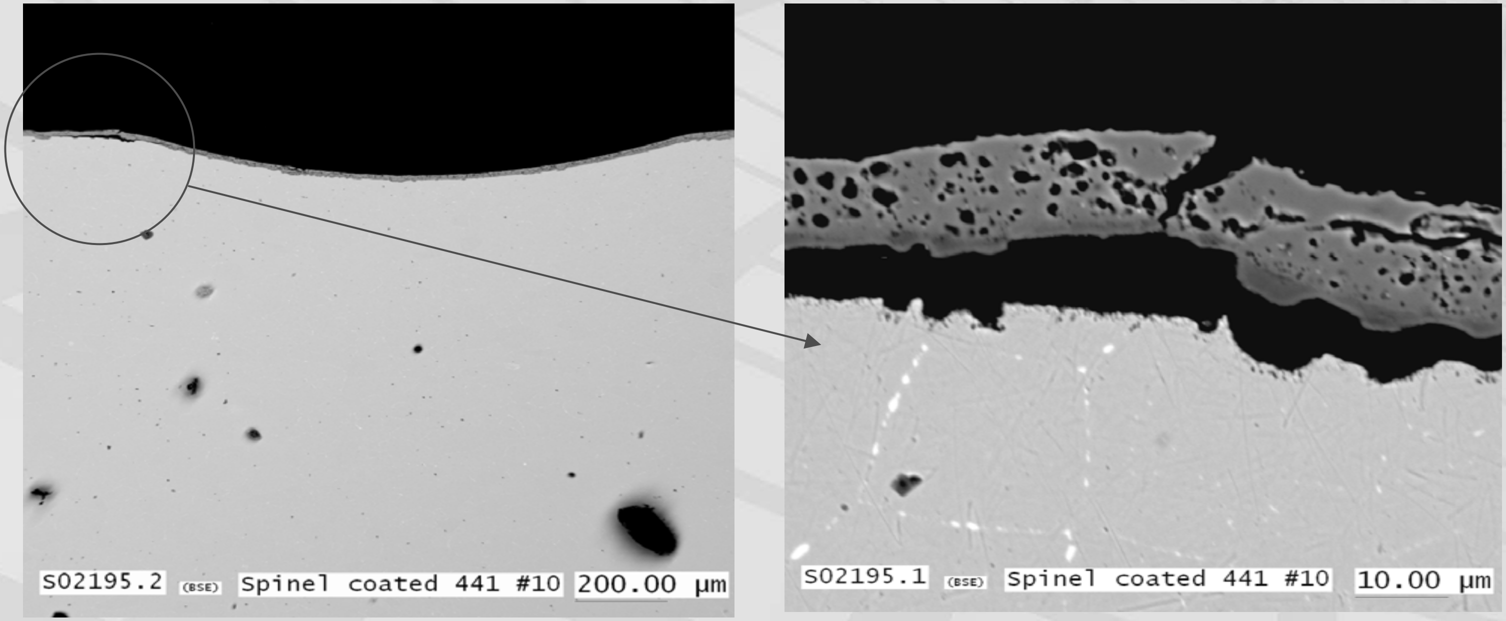
•Interfacial strength of oxide/spinel coating: 886MPa

Predicted maximum interfacial stress upon cooling

Coating	Coating: 10 um SS441: 1.6mm		Coating: 25 um SS441: 1.6mm		Coating: 50 um SS441: 1.6mm	
Scale	Scale/441	Scale/Coat	Scale/441	Scale/Coat	Scale/441	Scale/Coat
2 um	441 MPa	322 MPa	443 MPa	325 MPa	444 MPa	326 MPa
5 um	487 MPa	350 MPa	491 MPa	361 MPa	492 MPa	365 MPa
10 um	489 MPa	360 MPa	518 MPa	361 MPa	503 MPa	374 MPa
15 um	485 MPa	345 MPa	527 MPa	359 MPa	527 MPa	382 MPa

Experimental Indentation Tests on Coated SS441 Tri-Layer System

Spinel-coated SS441 illustrating failure occurring at oxide/substrate interface. Failure load was 150kgf utilizing 1/8" ball indenter.



- Failure consistently occurs at the oxide/SS441 interface

Life Improvement for Coated SS441 Tri-Layer System

- Reducing failure driving force:
  - By reducing the sheet thickness of SS441
- Improving interfacial adhesion strength:
  - Through Ce doped MC coating:
    - Currently being examined by materials/coating team;
  - Through surface modification:
    - Currently being examined;
  - Through grain boundary engineering:
    - Currently being examined.

Effect of Sheet Thickness on Interfacial Stresses for SS441

Predicted maximum interfacial shear stress for different substrate thickness

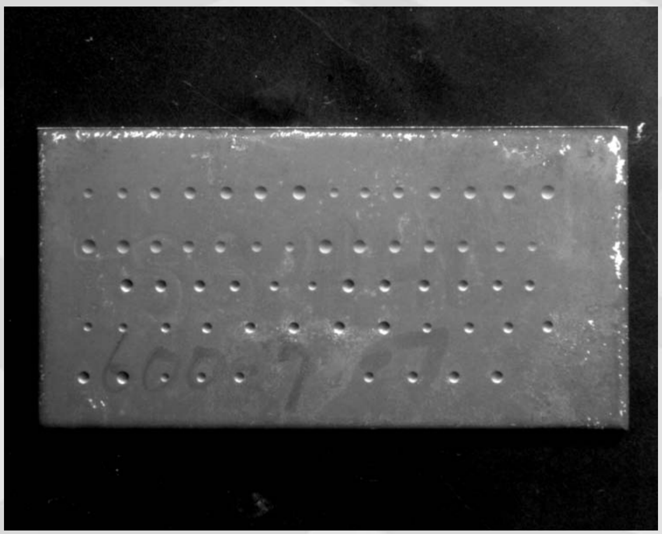
Substrate thickness	1.6mm		0.5mm	
Coating thickness	10 um		10 um	
Scale (um)	Scale/441	Scale/Coat	Scale/441	Scale/Coat
2	441 MPa	322 MPa	361 MPa	285 MPa
5	487 MPa	350 MPa	410 MPa	331 MPa
10	489 MPa	360 MPa	463 MPa	348 MPa
15	485 MPa	345 MPa	479 MPa	346 MPa

- Interfacial stresses at both interfaces decrease with decreasing SS441 thickness:
  - Interfacial failure driving force can be reduced by reducing the bulk thickness of SS441.

Interconnect Surface Modification Studies – Preliminary Results

- Polish SS441 surface to achieve similar roughness as Crofer;
- Oxidation at 800C for 600h, 900h, & 1200h;
- Indentation tests for oxidized samples:
  - Spalling vs no spalling
  - Observing similar oxide thickness when times were different

600h modified 441SS

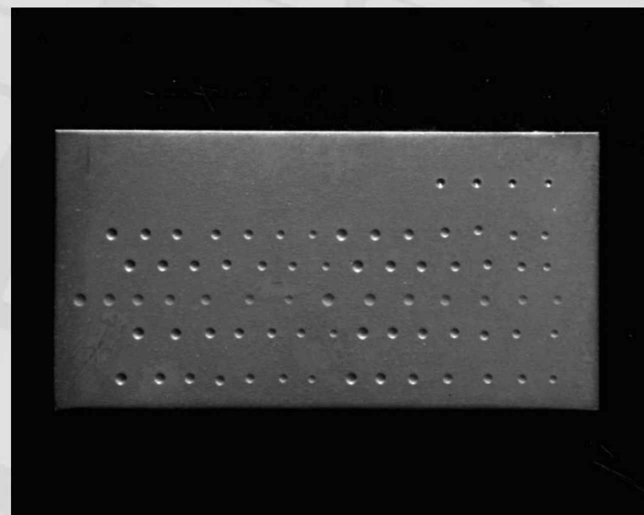


Edge spallation observed

900h modified 441SS

Specimen completely spalled

1200h modified 441SS



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Effect of Surface Finish on Oxide/SS441 Interfacial Strength – Preliminary Results

- Perform indentation test on 600h sample with 3.87micron oxide:
  - No spallation observed with 1/8” indenter
  - Spallation observed with 1/16” indenter

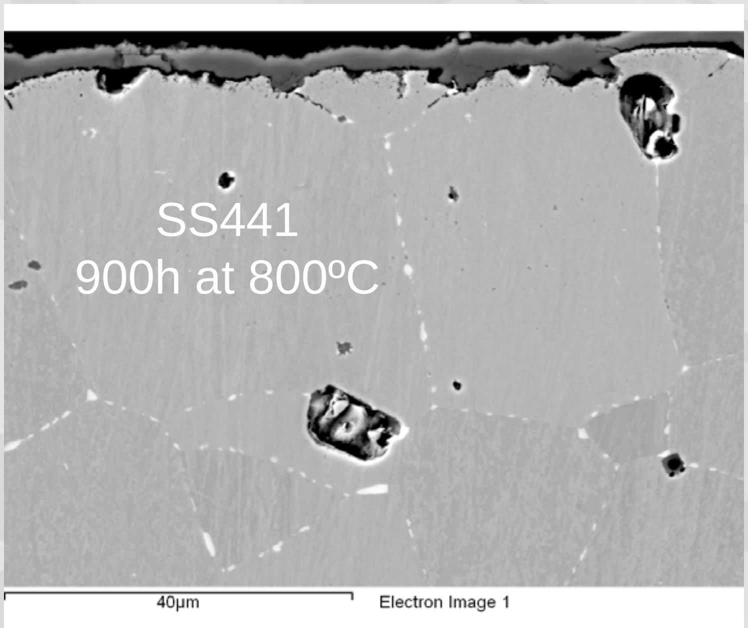
Indentation tests utilizing 1/16" Rockwell ball indenter; Oxidized 441 Samples Surface Modified

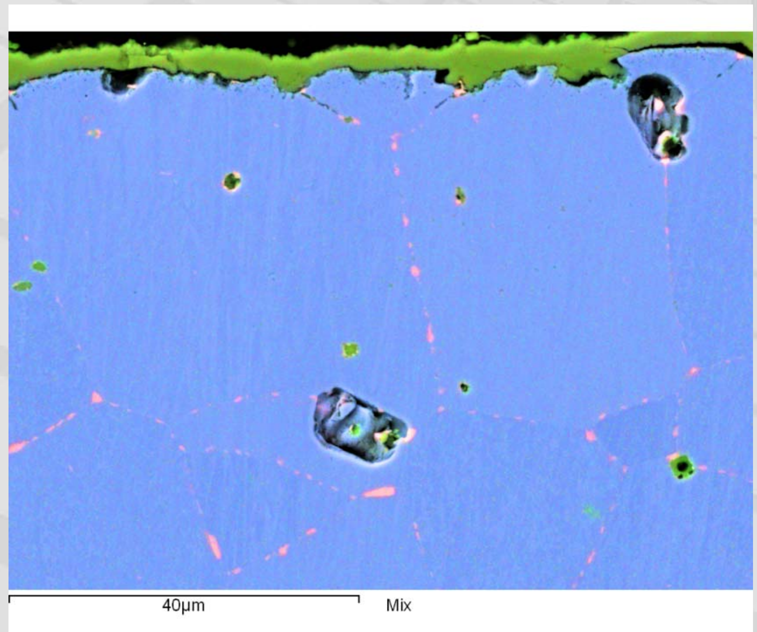
		Load (kgf)													
		60		75		90		100		115		130		150	
Spec.#	Scale Thickness (µm)	*No Spall*	*Spall*	*No Spall*	*Spall*	*No Spall*	*Spall*	*No Spall*	*Spall*	*No Spall*	*Spall*	*No Spall*	*Spall*	*No Spall*	*Spall*
1	3.87	4	0	4	0	2	3	2	3	1	4	0	5	0	4

- More consistent indentation results with polished SS441;
- Interfacial strength between oxide/SS441- surface modified: 394MPa, similar to that of Crofer.

Composition of SS441 & Crofer

Type	Cr	Mn	Ni	C	Al	Si	P	S	Ti	Nb	Re
T-441	17.6	0.33	0.20	0.010	0.045	0.47	0.024	0.001	0.18	0.46	
AL 430	17.0	≤1.0	≤0.75	≤0.12		≤1.0					
Crofer 22 APU	23.0	0.4-0.8		0.030	≤0.50	≤.50	0.020	0.050	≤0.2		0.04-0.20

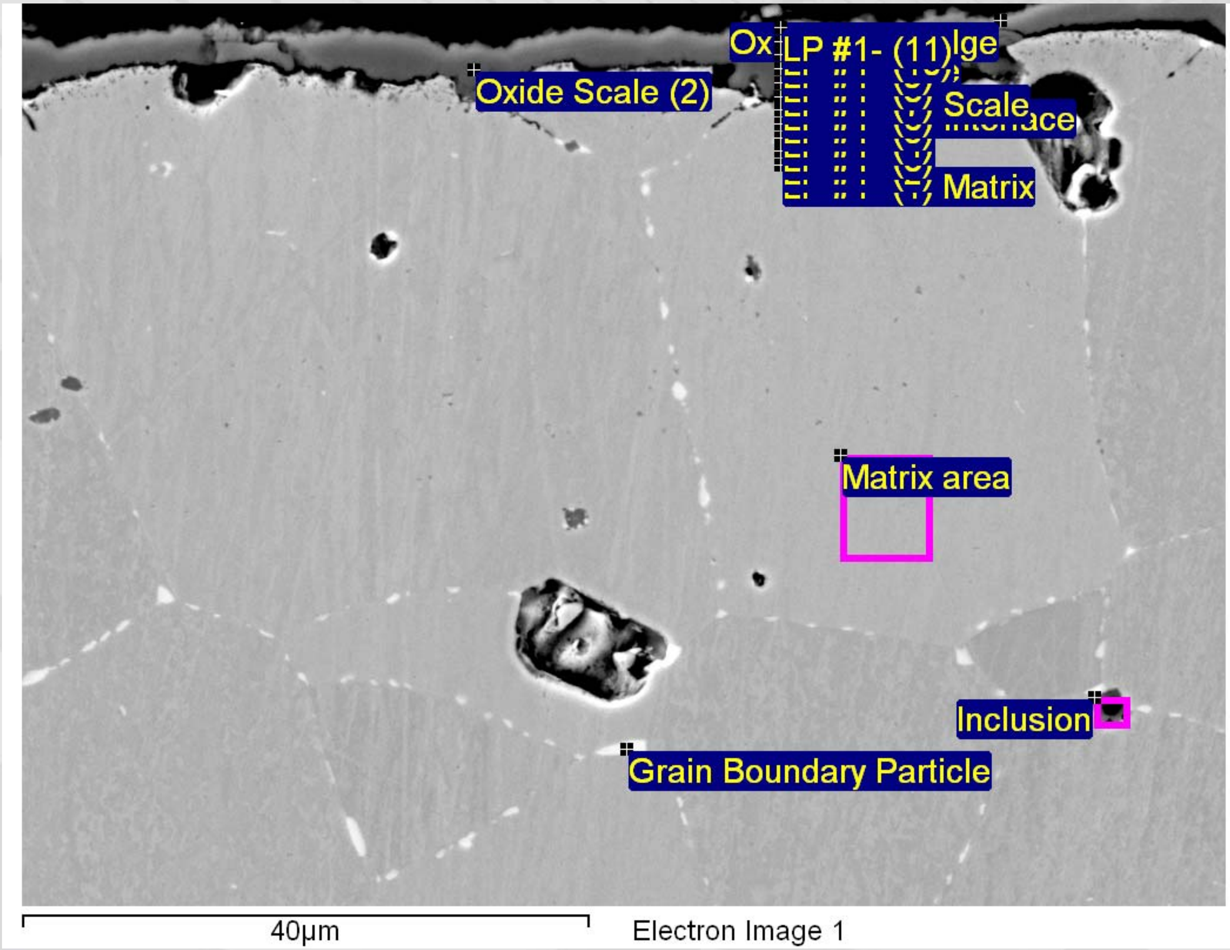




Visible grain boundary

Niobium: red; Titanium: green; Iron: blue.

EDS Identification Area



- Element identification taken along the thickness of the oxide scale, matrix of substrate, grain boundary, and inclusion

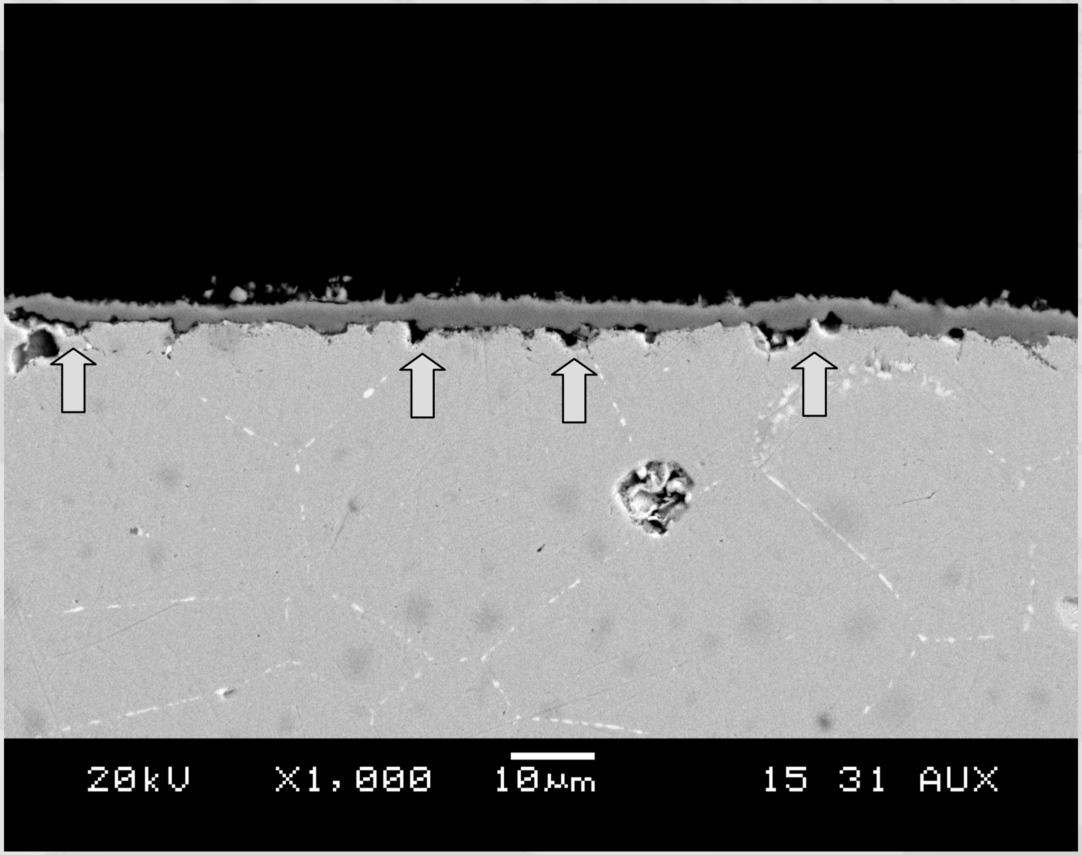
Distribution of Elements

Processing option: All elements analyzed (Normalized)

Spectrum	O	Al	Si	Ti	V	Cr	Mn	Fe	Nb
Oxide scale	90.22	0.00	0.00	0.00	0.00	**5.68**	0.00	4.10	0.00
Oxide Scale (2)	0.00	0.00	0.00	0.00	0.00	**40.44**	0.00	59.56	0.00
Oxide Scale edge	63.48	0.00	6.88	0.00	0.00	**17.25**	0.00	12.40	0.00
Matrix area	0.00	0.00	0.54	0.00	0.00	**17.45**	0.00	82.00	0.00
Grain Boundary Particle	1.23	0.00	1.87	0.78	0.13	**13.67**	0.27	65.74	16.31
LP #1-(1) Matrix	0.00	0.00	0.57	0.00	0.00	**17.08**	0.00	82.36	0.00
LP #1- (2)	0.00	0.00	0.59	0.00	0.00	**17.01**	0.00	82.40	0.00
LP #1- (3)	0.00	0.00	0.52	0.00	0.00	**17.24**	0.00	82.24	0.00
LP #1- (4)	0.00	0.00	0.61	0.00	0.00	**17.03**	0.17	81.69	0.49
LP #1- (5)	0.00	0.12	0.54	0.00	0.00	**17.07**	0.00	82.26	0.00
LP #1- (6) Interface	1.16	0.83	0.54	0.17	0.00	**16.91**	0.00	80.39	0.00
LP #1- (7) Scale	1.44	0.33	0.76	1.03	0.00	**16.99**	0.00	79.45	0.00
LP #1- (8)	13.91	0.96	2.60	5.36	0.17	**20.18**	0.30	54.84	1.67
LP #1- (9)	36.61	0.77	0.72	3.85	0.25	**49.70**	1.68	5.07	1.36
LP #1- (10)	37.58	1.20	0.27	3.41	0.15	**55.14**	0.84	1.17	0.25
LP #1- (11)	37.99	0.23	0.00	1.90	0.00	**58.99**	0.37	0.53	0.00
Inclusion	28.35	3.27	1.17	35.45	0.00	**4.88**	0.00	20.10	6.78

All results in weight%

Observations from EDS

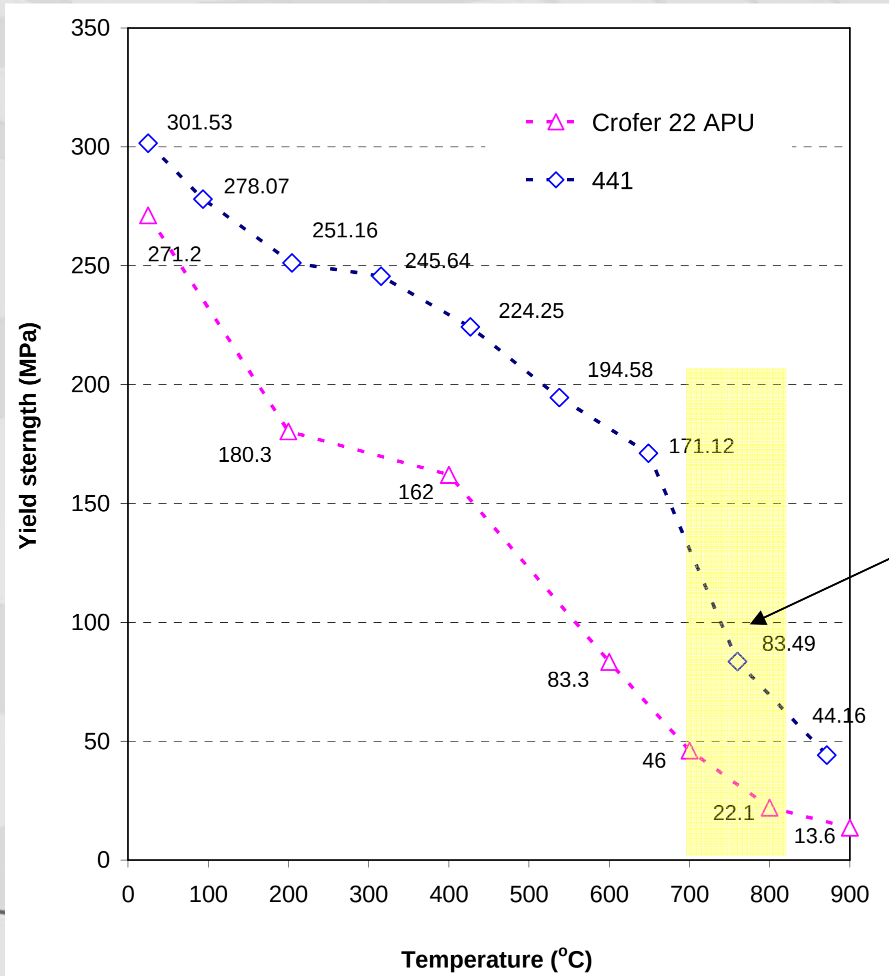


- Cr content in grain boundary is lower than substrate and oxide scale
  - Preferential diffusion of Cr: faster in grains, slower toward grain boundaries?
  - Non-uniform oxide growth at the grain boundary and free surface junction: potential sites for initial de-cohesion.

Effects of Nb at Grain Boundary

Yield strength vs. temperature

Annealed, 0.020'' (0.5 mm)



After Allegheny Ludlum and ThyssenKrupp

- Grain boundary is Nb/Si/Ti rich – Consistent with experimental TEM measurement
  - Poor grain boundary cohesion due to Nb(1)
  - Increasing Nb reduces hot ductility at 800ºC
  - Consistent with experimental yield strength comparison between SS441 and Crofer at 800ºC

(1) Chiaki OUCHI and Kazuaki MATSUMOTO, "Hot Ductility in Nb-bearing High-strength Low-alloy Steels", Transactions ISIJ, Vol. 22, pp. 181-189, 1982.

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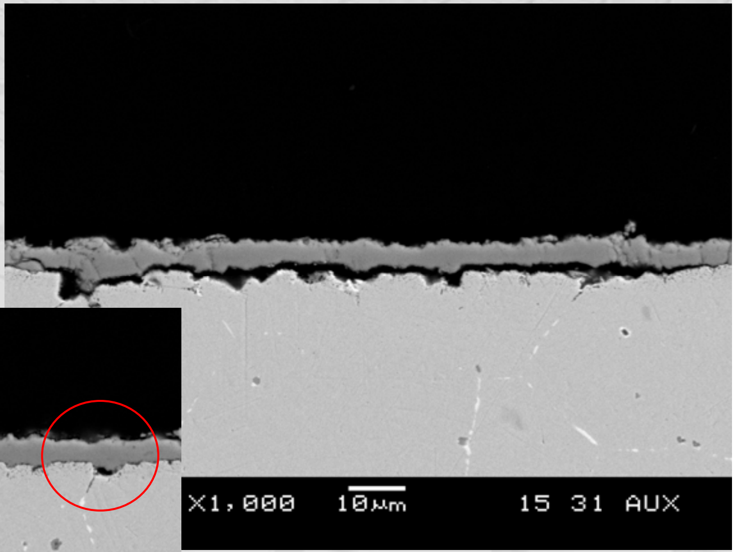
Cross Section of Oxidized SS441(as-Received)



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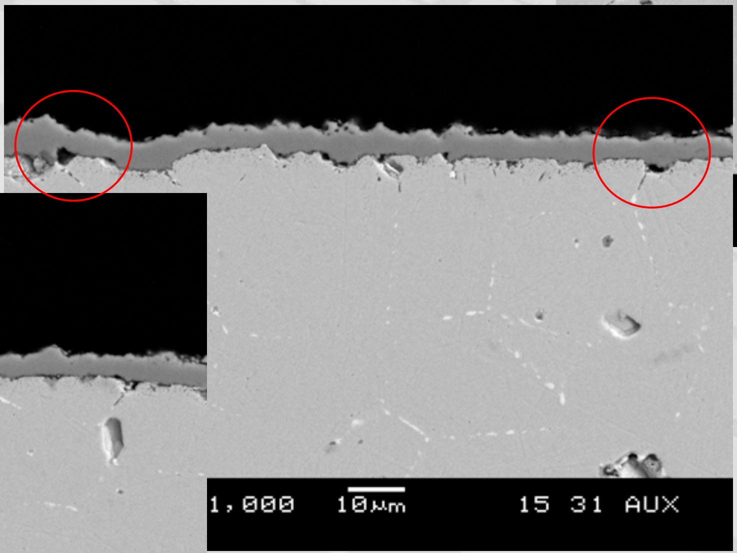

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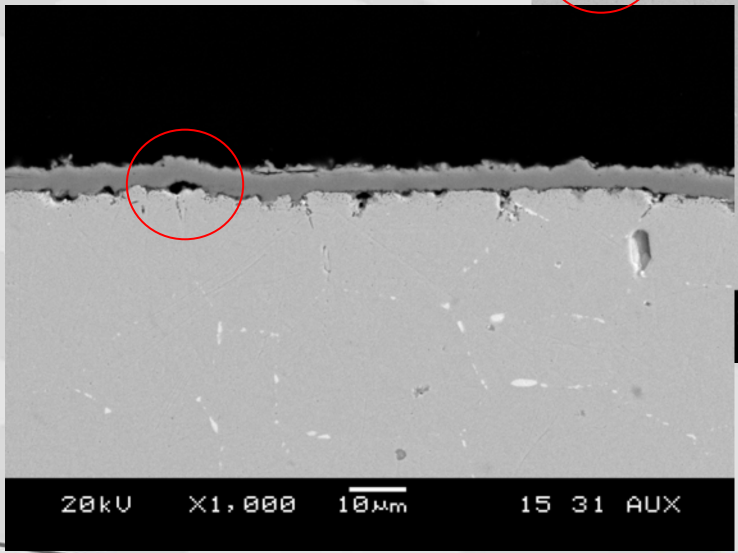

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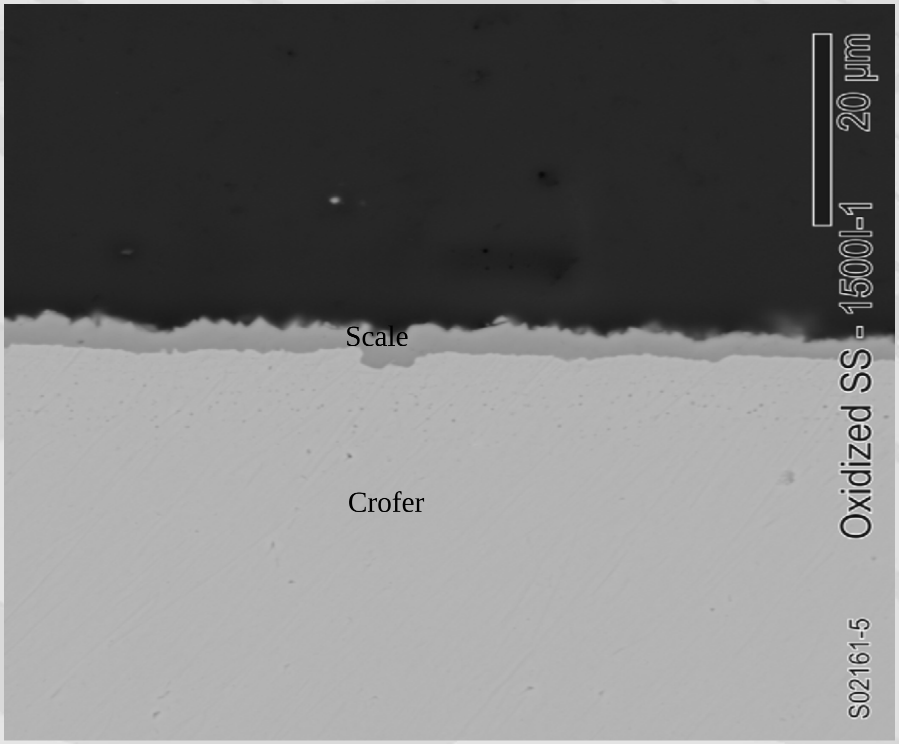
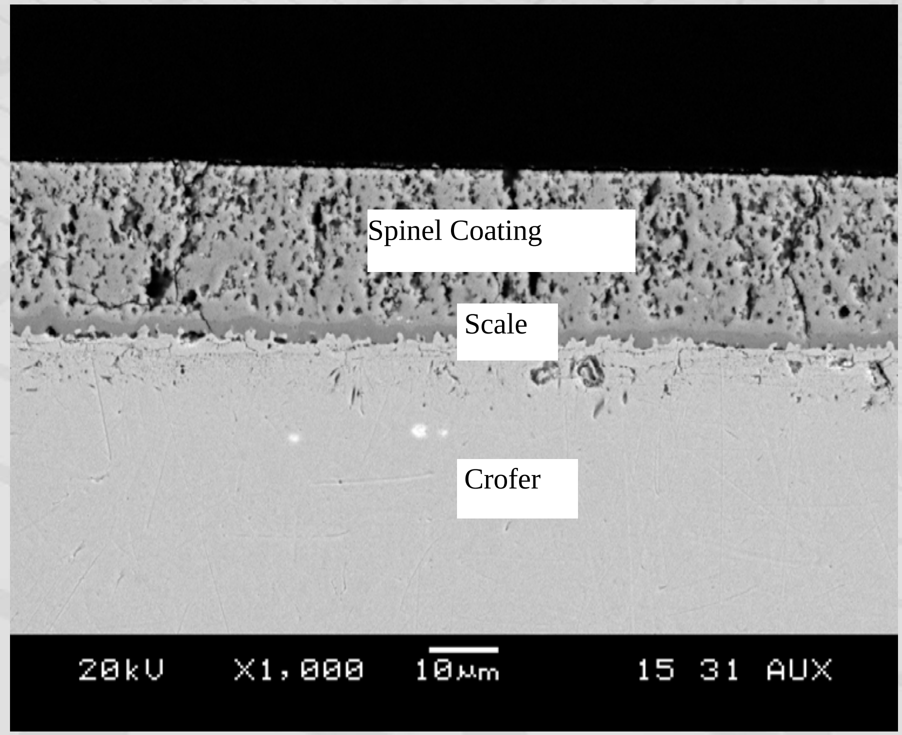
Comparison with Crofer



Bare oxidized



Spinel coated oxidized

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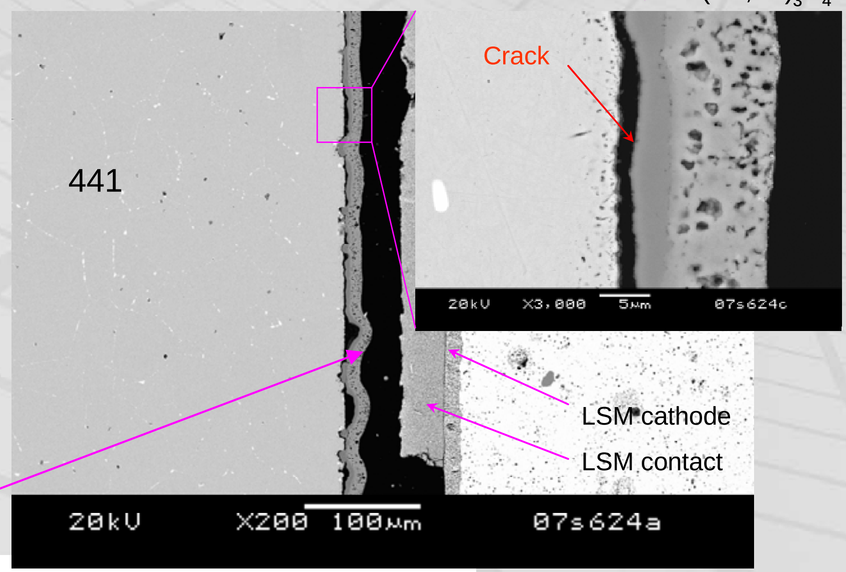
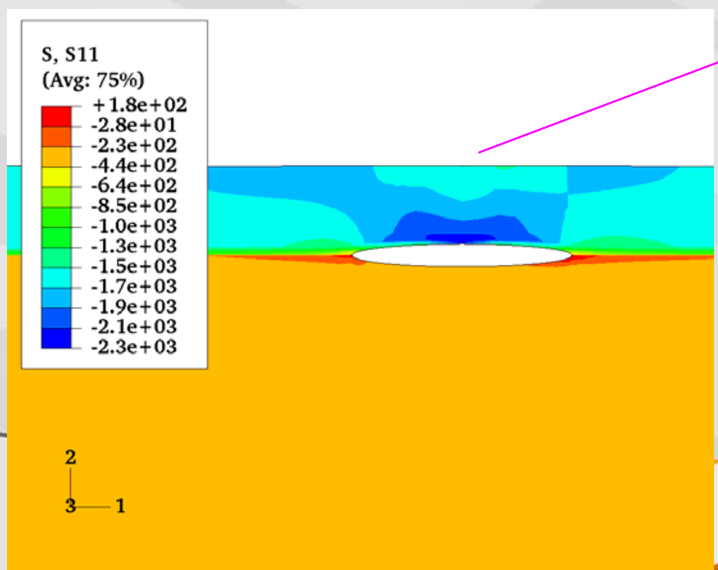
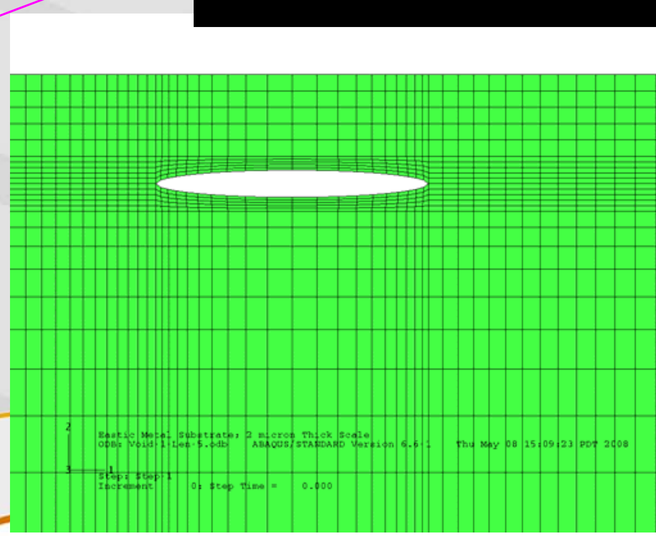
Effect of Interfacial Voids on Interfacial Shear Strength during Cooling

- Calculating cooling-induced stresses in the scale:
  - Thickness of scale: 2 um
  - Crack length: 5 um length
  - Crack height: 0.5 um
- Failure driving force: buckling of the free-standing scale
- Consistent with experimental observations





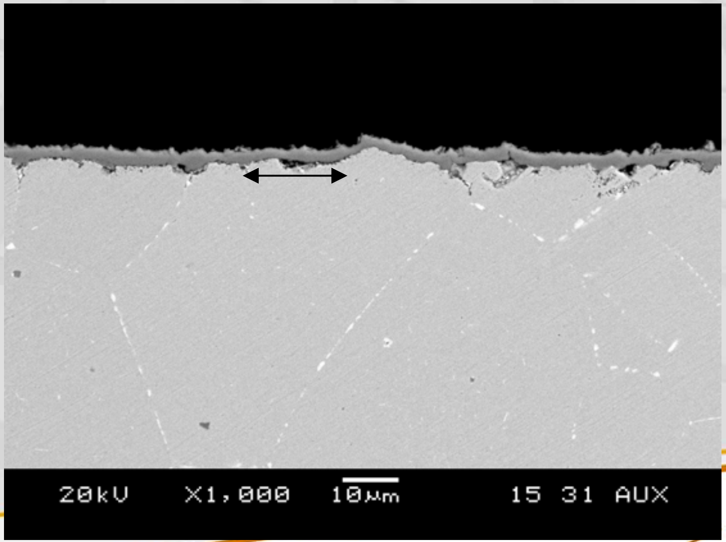


Critical Size of Interfacial Defects during Cooling Process

- For circular disk crack, the critical stress of buckling under compressive stress is calculated as[(1)]

$$\sigma_{cr} = 1.2235 \frac{E}{1-\nu^2} \left(\frac{H}{a} \right)^2$$

- Assume thickness of scale is 2 um, crack length is 10 um, and the height of crack is 1 um, the critical compressive stress is obtained as $\sigma_{cr} = 7.3\text{GPa}$



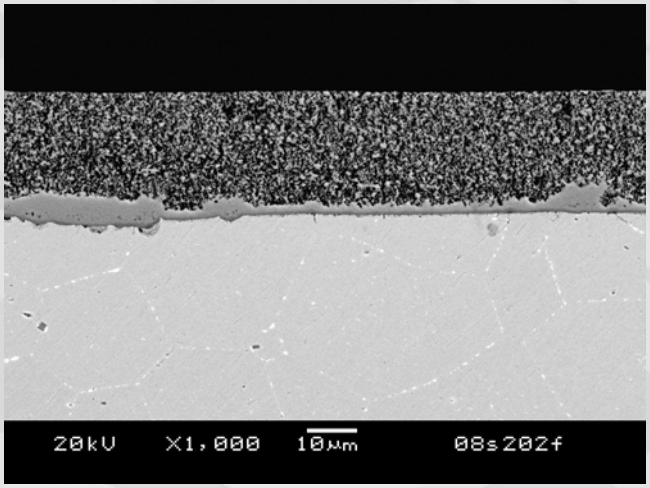
- Using the cooling induced stress of ~3 GPa, the critical size of interfacial crack will be

$$a_{cr} = 15.6\text{um}$$

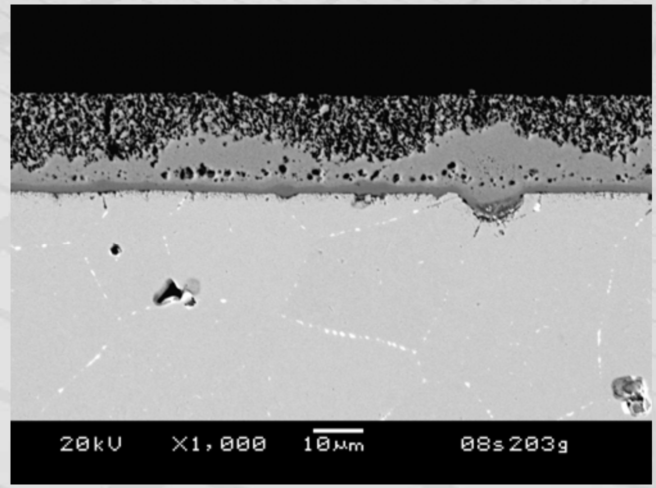
(1) Hutchinson, J.W. and Suo, Z., Mixed Mode Cracking in Layered Materials, *Advances in Applied Mechanics*, Vol. 29, pp. 64-187, 1992.

Interconnect Experiments – Ce-Spinel Coated Samples

Specimen 441 Ce-3 – 200h @ 800C



Specimen 441 Ce-8 – 1200h @ 800C



- No failures observed with a 1/8” indenter in comparison to unmodified spinel-coated 441

Spinel-coated 441 SS

441-10
800C @ 1200h
12.69
1.53
S02195.4 & S02195.5

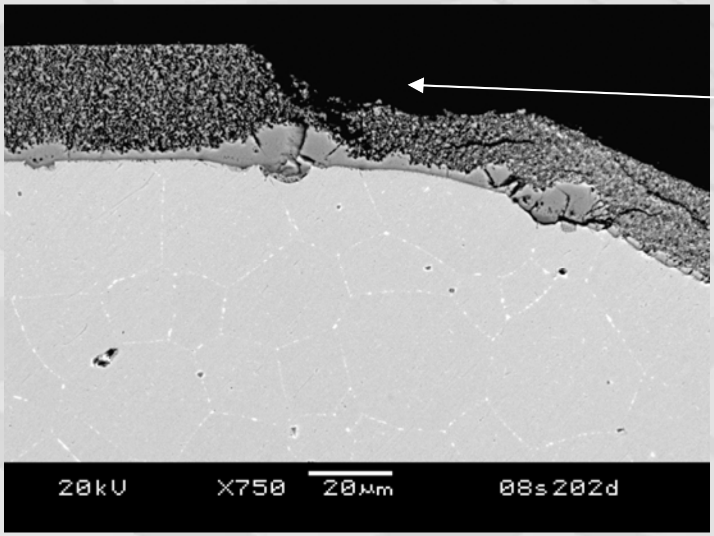
Force	No Spall	Spall
60	1	0
75	1	0
90	1	0
100	2	0
115	3	0
130	2	1
150	2	1

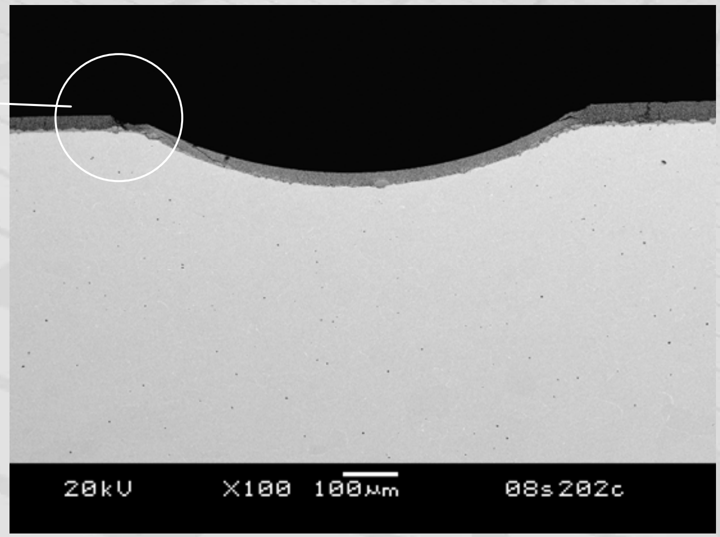
Ce- doped spinel-coated 441 SS

441 Ce-8
800C @ 1200h

Force	No Spall	Spall
60	2	0
75	2	0
90	3	0
100	3	0
115	3	0
130	3	0
150	3	0

Failure of 200h Ce-Spinel Coated SS441 Specimen





- Failure observed between coating and rxn layer interface
- No failures observed with 1/8" ball indenter
- Failure observed at 130kgf with 1/16" ball indenter

	441 Ce-3 800C @ 200h
Coating Thickness (um):	
Oxide Thickness (um):	0.51
Rxn Layer Thickness (um):	
Image:	08s202e & 08s202f

Force	No Spall	Spall
60	3	0
75	3	0
90	3	0
100	3	0
115	3	0
130	2	1
150	0	3

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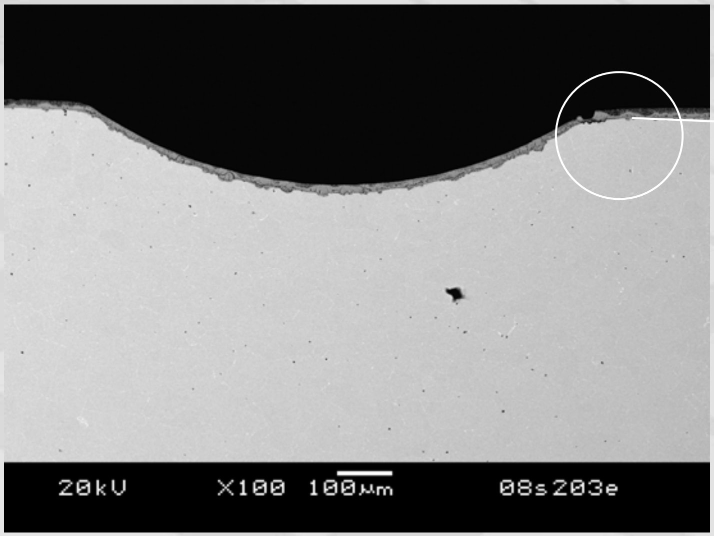
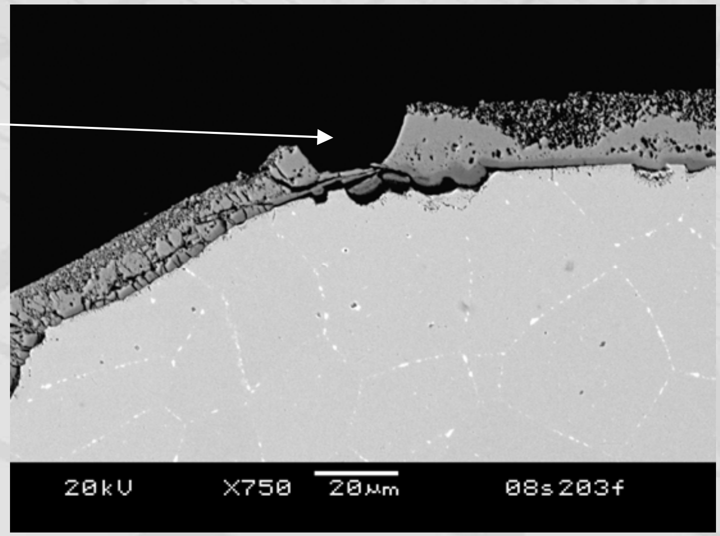
Failure of 1200h Ce-Spinel Coated SS441 Specimen





- Failure location difficult to assess
- No failures observed with 1/8" ball indenter
- Failed at all loads with 1/16" ball indenter

441 Ce-8
800C @ 1200h

Coating Thickness (um):
Oxide Thickness (um):
Rxn Layer Thickness (um):
Image: 08s203d & 08s203g

Force	No Spall	Spall
60	0	4
75	0	3
90	0	3
100	0	3
115	0	3
130	0	3
150		-

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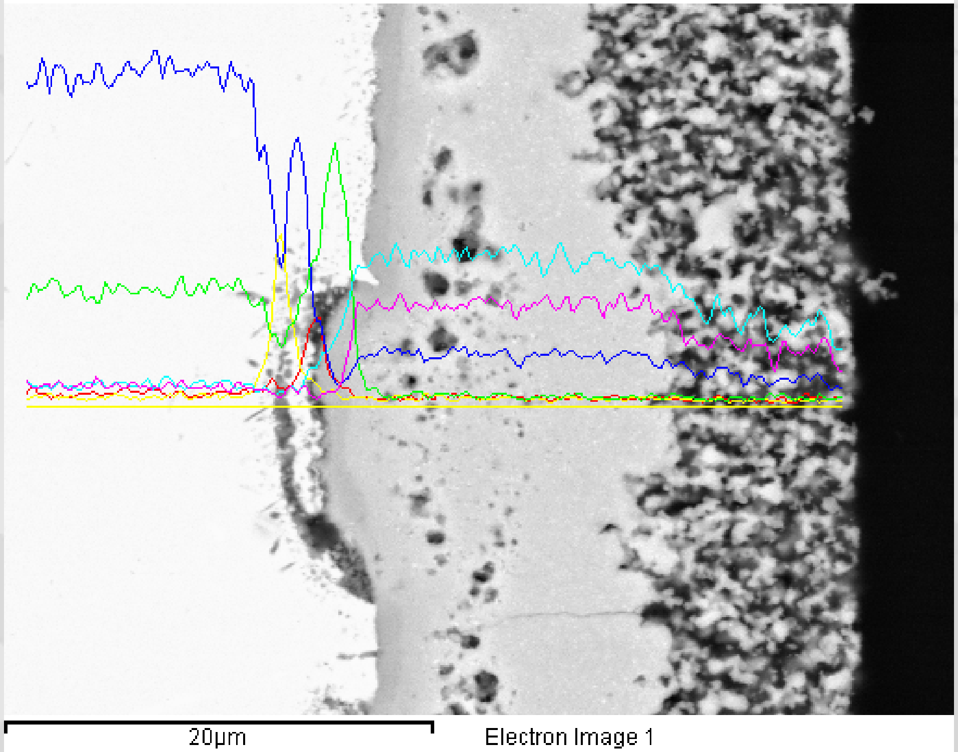
EDS of Ce-doped Spinel Coated SS441 Specimen



- With Ce-doped MC coating, a sub-layer rich in Ti and Si is formed between the SS441 and scale:
  - Filling in the gap previously observed on the oxide/SS441 interface
  - Reducing interfacial stress during cooling

Silicon: red;
Chromium: green;
Iron: blue;
Yellow: titanium
Pink: cobalt
Cyan: Manganese

Next Steps

- Quantify interfacial strength for SS441/oxide/Ce-MC tri-layer system
  - Indentation tests for various oxidized samples;
  - Grain boundary composition characterization with TEM – collaboration with experimental program;
  - Identify possible grain-boundary strengthening mechanism with Ce;
  - Nano-indentation tests to quantify grain boundary strength.
- Quantify subscale growth kinetics for various Ce-MC coating thickness – Collaboration with experimental program
- Coated SS441 life prediction with improved scale/substrate adherence